2553

Ascorbate and Tripolyphosphate in Cured, Cooked, Frozen Pork

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Frozen, cured, cooked pork samples containing sodium tripolyphosphate and twice the legal limit of sodium ascorbate (0.108%) were protected from salt-catalyzed lipid oxidation for more than one year of storage. In contrast, samples with 0.054% sodium ascorbate were rancid at four months. Ascorbate loss was related to increase in lipid oxidation. Rapid peroxidation took place in the 0.054% sodium ascorbate sample when the last bit of ascorbate disappeared. Loss of ascorbate was a problem only in samples containing both nitrite and salt. The addition of a larger quantity of ascorbate (>0.054%) was recommended for cooked cured products to be frozen. Tripolyphosphate concentration did not change significantly with storage.

In a recent communication (*8*), the authors noted that frozen, cured, cooked pork samples containing sodium tripolyphosphate and sodium ascorbate were protected from oxidative rancidity for several months of storage. However, at close to a year, these samples were more highly rancid than untreated cured controls. The increase in lipid oxidation was sudden and drastic. A similar increase in rancidity did not occur in uncured samples of the same meat after more than two years of frozen storage.

Tripolyphosphate alone was not protective for frozen cured pork. Ascorbate alone gave some protection, but was more effective in combination with tripolyphosphate—during the effective period.

On the basis of this information, possibly the curing ingredients, NaCl and $NaNO_2$, were fostering removal of the protective factor. After exhaustion of the inhibitor, the previously undiminished lipid material would be subject to rapid peroxidation. Mahon (*5*) has indicated that hydrolysis of tripolyphosphate, due to enzyme action, is very rapid in raw meats. Further hydrolysis may occur during freezer storage in the presence of curing salts. The orthophosphate which would ultimately result is not effective as an antioxidant in uncured meats (*6*). Nitrite and ascorbic acid are known to react in curing mixtures (*2*), and Hougham (*3*) found that ascorbic acid caused loss of free nitrite in hams. Ascorbic acid loss also may occur.

The work reported was designed to investigate loss of ascorbate and tripolyphosphate in pork containing various combinations of curing and "protective" ingredients while following the pattern of lipid oxidation.

Methods

Preparation of Meat. The general procedure of handling has been reported (*8*). All of the fresh pork ham used in this work was purchased, ground, and processed at one time. The additives consisted of various combinations of the following: 0.5% sodium tripolyphosphate, 0.054 or 0.108% sodium ascorbate, 0.03% sodium nitrite, and 4% sodium chloride. Since hydrolysis of tripolyphosphate is reported to be rapid in raw meat (*5*), one variation was prepared at a time, and a standard time of 6 minutes was used for mixing, weighing into cans, sealing, and putting into the autoclave (free-flowing steam) for heating to an internal temperature of 70° C. The meat was placed in polyethylene bags which were heat-sealed and stored at 0° F. (−18° C.).

Lipid Oxidation. The 2-thiobarbituric acid (TBA) test was used to measure malonaldehyde in all samples (*9*). Duplicate determinations were made and the average is reported as TBA number—i.e., milligrams of malonaldehyde per 1000 grams of meat.

Phosphate Analysis. The paper chromatographic technique described by Karl-Kroupa (*4*) was used for assay of tripoly-, pyro-, and orthophosphates. Duplicate 5-μl. samples of liquid pressed from 20-gram portions of meat were used for assay. After development, the resulting spots were circled and their areas (square millimeters) obtained with an Ott compensating planimeter. When 2 to 12 μg. of tripolyphosphate were deposited on the starting line, the size of the resulting spots was related to the amount of phosphate present.

Ascorbate Assay. The photometric method of ascorbic acid assay (*1*) was used with modification. ince Hollenbeck and Monahan (*2*) pointed out that reaction between sodium ascorbate and $NaNO_2$ is negligible at pH 6 to 7, the dye (2,6-dichloroindophenol) was dissolved in 0.1*M* phosphate buffer, pH 6.7, in place of the more usual metaphosphoric acid. Dye solution, against a phosphate buffer blank, gave a broad absorbance peak between 600 and 615 mμ on a Bausch and Lomb 505 recording spectrophotometer. Routine measurements were made at 605 mμ with a Bausch and Lomb Spectronic 20 colorimeter. Approximately 10 mg. of dye were added to 1 liter of buffer, and sufficient dilution was made to obtain an absorbance of 0.640 or slightly lower at 605 mμ.

Before each assay, a standard curve was determined with freshly prepared aqueous sodium ascorbate solution (0.01 to 0.05 mg. per ml.). For assay, a 10-gram

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portion of sample was blended with 40 ml. of distilled water for 1 minute. The slurry was filtered and a 1-ml. sample taken. This was diluted to 5 ml. with distilled water, and 1-ml. aliquots were used for the assay. Duplicate determinations were carried out, and the data were calculated as milligrams per 100 grams of meat. The per cent loss was calculated on the basis of the amount of sodium ascorbate actually added to the meat—54 or 108 mg.

Results and Discussion

As shown in Figure 1, rancidification of the cured sample containing tripolyphosphate and ascorbate follows the pattern previously described (*8*). Again,

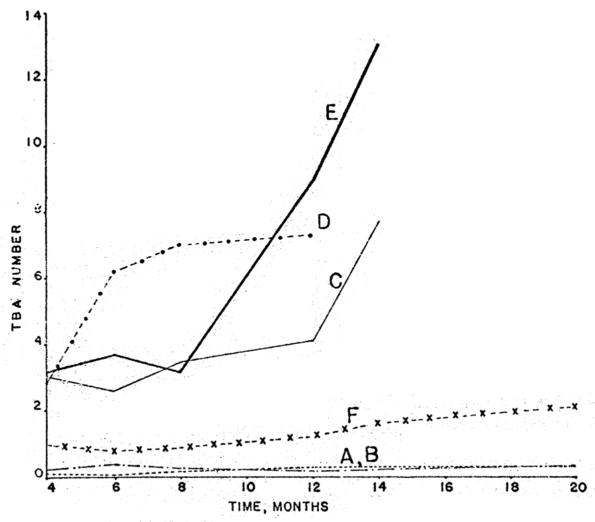

Figure 1. Development of rancidity in frozen, cured, cooked pork

A. Nitrite + tripolyphosphate + ascorbate
B. Sodium chloride + tripolyphosphate + ascorbate
C. Nitrite + sodium chloride + ascorbate
D. Nitrite + sodium chloride + tripolyphosphate
E. Nitrite + sodium chloride + tripolyphosphate + ascorbate
F. Nitrite + sodium chloride + tripolyphosphate + 2 ascorbate

tripolyphosphate alone was not as protective as when in combination with ascorbate—until 8 months of frozen storage had elapsed. In this case, ascorbate alone was more protective than the combination but is known to behave erratically when added to meat (*7*). However, in all cases the meat had TBA numbers in the vicinity of 3 after 4 months of storage, and typical rancid odors were present. The cured sample containing tripolyphosphate and double ascorbate had TBA numbers in the vicinity of 1 until a year of storage had passed, after which there was a gradual increase to 2 at 20 months. The samples containing salt and nitrite separately with the antioxidant combination were completely protective.

No objective measurements of cured meat color were made, but visual observation supported the results reported previously—i.e., any antioxidant treatment which retarded lipid oxidation also retarded pigment loss. The cured sample containing both tripolyphosphate and ascorbate had faded markedly after 4 months. The sample with $NaNO_2$ alone and that with double ascorbate still had good color after 20 months of frozen storage. All samples gave positive sulfhydryl tests throughout the course of the experiment. This, too, is in agreement with previously reported results (*8*). Free nitrite gradually disappeared as the experiment progressed.

The size of the tripolyphosphate spots was not related to the TBA numbers, and there appeared to be no significant change with storage. Although this method of assay is not a precise one, the conclusion that loss of tripolyphosphate is not responsible for the oxidative changes observed in frozen cured pork seems reasonable.

Ascorbate loss does appear to be related to increases in lipid oxidation in cured samples. As seen in Figure 2, ascorbate loss takes place most rapidly in the cured sample containing tripolyphosphate and ascorbate. However, the TBA number in this sample changes little between 4 and 8 months, while ascorbate is reduced from 18 to 5 mg. Rapid lipid oxidation sets in only when the last bit of ascorbate disappears. The sample containing twice the legal limit for ascorbate (0.054% is limit) is

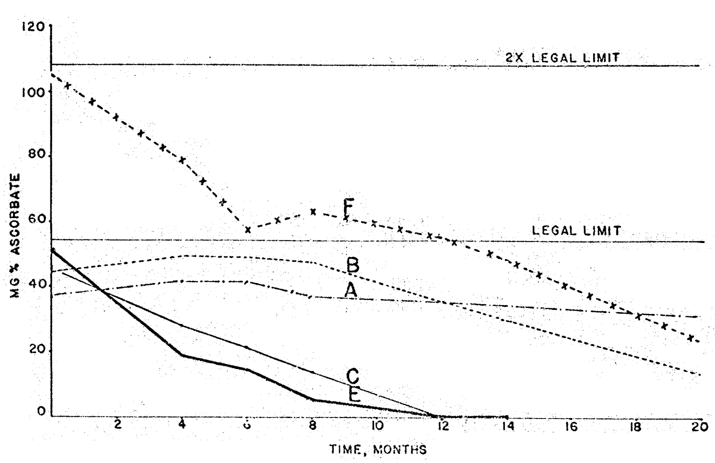

Figure 2. Loss of ascorbate in frozen, cured, cooked pork

A, B, C, E, F as in Figure 1

only starting to exhibit rancidity at 14 and 20 months when more than half of the ascorbate is gone. Ascorbate appears to be lost at about the same rate in both samples (54 mg. per year). The double ascorbate sample would be expected to begin oxidizing rapidly once the last bit of its ascorbate is lost. This sample contains more ascorbate at 20 months than the 0.054% ascorbate sample at 4 months. Ascorbate loss does not take place to any great extent in the samples containing $NaNO_2$ and NaCl separately, although the content of the salted sample falls off at 20 months.

Loss of ascorbate appears to be a problem only in samples containing both nitrite and salt. Although nitrite and ascorbate are known to be antagonistic, nitrite alone does not destroy a large quantity of ascorbate (44% loss in 20 months). In curing brines, salt stabilized ascorbic acid against oxidation (*2*), probably by reducing oxygen solubility. An explanation of the reported observations is not apparent at this time.

Clearly, ascorbate plays an important role in maintaining the quality of frozen, cooked, cured pork containing sodium tripolyphosphate. Since the compound is so readily destroyed in meats containing curing salts, the authors recommend that a larger quantity (more than 0.054%) of ascorbate be allowed in such products to be frozen. Application of this to commercially produced sausage and prepared ham dinners would be of interest.

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